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10/525730
PCT/GB 2003/003438



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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02358020.2

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R C van Dijk



Anmeldung Nr:
Application no.: 02358020.2
Demande no:

Anmeldetag:
Date of filing: 29.08.02
Date de dépôt:

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
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Polymerisation process

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C08F10/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

POLYMERISATION PROCESS

The present invention relates to polymerisation processes in particular to processes for the polymerisation of olefins and in particular to processes using supported metallocene catalysts. The present invention is particularly directed to gas phase polymerisation processes.

5 In recent years there have been many advances in the production of polyolefin homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature. There have been developed several different families of metallocene complexes. In
10 earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed, examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes
15 the metal atom eg. zirconium is in the highest oxidation state.

Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

20 The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are

borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-borates. Catalyst systems incorporating such borate activators are described in EP 561479, EP 418044 and EP 551277.

5 The above metallocene complexes may be used for the polymerisation of olefins in solution, slurry or gas phase. When used in the gas phase the metallocene complex and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245,
10 WO 96/04318, WO 97/02297 and EP 642536.

WO 98/27119 describes supported catalyst components comprising ionic compounds comprising a cation and an anion in which the anion contains at least one substituent comprising a moiety having an active hydrogen. In this disclosure supported metallocene catalysts are exemplified in which the catalyst is prepared by treating the
15 aforementioned ionic compound with a trialkylaluminium compound followed by subsequent treatment with the support and the metallocene.

Supported metallocene catalysts have been primarily used for the gas phase processes. In such processes various additives may be added to the gas phase in order to improve the process or the characteristic of the resultant polymers.

20 For example EP 781300 describes the use of small amounts of scavenger in gas phases processes catalysed by metallocenes to reduce the tendency of fouling and sheeting. Typical scavengers described for this purpose include organometallic compounds such as trialkylaluminium compounds and in particular triethylaluminium. The scavengers may be used during start-up or added continuously in specific amounts
25 during the polymerisation process. The scavenger may be introduced directly or

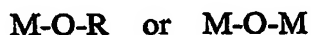
indirectly into the reactor or into any external means which allows the scavenger to enter the reactor. The metallocenes systems exemplified are those based on bis(cyclopentadienyl) complexes for example bis(1,3-dimethyl-n-butyl)cyclopentadienyl) zirconium dichloride/methylaluminoxane systems.

30 Such trialkylaluminium compounds may however deactivate certain metallocene catalyst systems for example metallocenes comprising monocyclopentadienyl complexes.

We have now surprisingly found that gas phase processes catalysed by certain metallocenes may be improved by the addition of certain organometallic compounds into the gas phase reactor.

5 Improved poison scavenging may be observed as well as advantages in activity profiles, catalyst activity and product characteristics.

Thus according to the present invention there is provided a gas phase process for the homopolymerisation of ethylene or the copolymerisation of ethylene and α -olefins, said process being carried out in the presence of a metallocene catalyst system comprising (a) a metallocene complex and (b) an ionic activator said process
10 *characterised* in that an organometallic compound of a Group III metal comprising the group



where M is the Group III metal and R is a hydrocarbyl group is added to the gas phase reactor.

15 Preferred organometallic compounds are those where the metal M is aluminium or boron and the hydrocarbyl group is a C1-C4 alkyl group for example methyl or isobutyl.

Preferred organometallic compounds in which the metal is aluminium are aluminoxanes.

20 Suitable aluminoxanes include those well known in the art for example methyl aluminoxane (MAO). A particularly preferred aluminoxane for use in the process of the present invention is tetraisobutylaluminoxane (TiBAO).

Other suitable organometallic compounds are alkoxides for example diethylaluminiummethoxide.

25 The organometallic compound may be added directly to the gas phase reactor or preferably may be injected into the reactor together with the metallocene catalyst system for example in a suitable solvent.

The preferred molar ratio of organometallic compound added to the gas phase reactor to metallocene complex is in the range 100000:1 to 1:100. A preferred range is
30 from 50000:1 to 1:10 and the most preferred range is from 500:1 to 1:10.

The metallocene complex may comprise for example a traditional bis(cyclopentadienyl) metallocene complex or more preferably a monocyclopentadienyl complex having a 'constrained geometry' configuration.

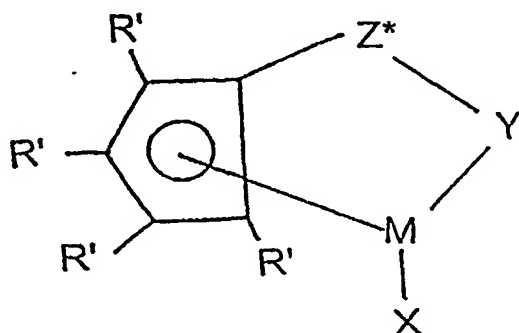
Bis(cyclopentadienyl) metallocene complexes may be represented by those disclosed in EP 129368 or EP 206794. Such complexes may be unbridged e.g. bis(cyclopentadienyl) zirconium dichloride or bridged e.g. ethylene bis(indenyl) zirconium dichloride. Other suitable metallocene complexes are those

5 bis(cyclopentadienyl) diene complexes described in WO 96/04290.

Examples of monocyclopentadienyl complexes suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277.

Particularly suitable monocyclopentadienyl complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

10 Particularly preferred metallocene complexes for use in the process of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen,

15 hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen

20 atoms, which forms a π complex with M;

Y is -O-, -S-, -NR*-, -PR*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z* is SiR^*_2 , CR^*_2 , $\text{SiR}^*_2\text{SiR}^*_2$, $\text{CR}^*_2\text{CR}^*_2$, $\text{CR}^*=\text{CR}^*$, $\text{CR}^*_2\text{SiR}^*_2$, or

GeR*₂, wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when
5 R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

Examples of suitable X groups include s-trans- η^4 -1,4-diphenyl-1,3-butadiene, s-trans- η^4 -3-methyl-1,3-pentadiene; s-trans- η^4 -2,4-hexadiene; s-trans- η^4 -1,3-pentadiene; s-trans- η^4 -1,4-ditolyl-1,3-butadiene; s-trans- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene; s-
10 cis- η^4 -3-methyl-1,3-pentadiene; s-cis- η^4 -1,4-dibenzyl-1,3-butadiene; s-cis- η^4 -1,3-pentadiene; s-cis- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire
15 C₅R'₄ group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, tetrahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C₁₋₁₀ hydrocarbyl.

20 Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the process of the present invention are those disclosed in the aforementioned WO 95/00526 and are incorporated herein by reference.

25 A particularly preferred complex for use in the process of the present invention is (t-butylamido) (tetramethyl- η^5 -cyclopentadienyl) dimethyl silanetitanium - η^4 -1,3-pentadiene

The ionic activators typically comprise a cation and an anion for example those described in EP 277003, EP 277004 and EP 561479.

30 The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

5 The preferred ionic activators are those wherein the cation of the ionic activator comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate..

Typical borates suitable as ionic activators include:

10 triethylammonium tetrphenylborate
triethylammonium tetrphenylborate,
tripropylammonium tetrphenylborate,
tri(n-butyl)ammonium tetrphenylborate,
tri(t-butyl)ammonium tetrphenylborate,
N,N-dimethylanilinium tetrphenylborate,
N,N-diethylanilinium tetrphenylborate,
15 trimethylammonium tetrakis(pentafluorophenyl) borate,
triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
20 N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

A most preferred type of activator suitable for use with the metallocene complexes of the present invention comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

25 ~~Suitable activators of this type are described in WO 98/27119 the relevant~~
portions of which are incorporated herein by reference.

Particular preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-
30 hydroxyphenyl) borate.

With respect to this preferred type of ionic activator, the reaction product of an alkylammonium tris(pentafluorophenyl)-4-(hydroxyphenyl) borate and an organometallic

compound, for example triethylaluminium may be most suitable.

It is most preferred that the metallocene catalyst system is supported.

Suitable support materials include inorganic metal oxides or alternatively polymeric supports may be used.

5 The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include Crosfield ES70 and Davison 948 silicas.

The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material.

10 Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure.

15 The support material may be further combined with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

The support material is pretreated with the organometallic compound at a temperature of -20°C to 150°C and preferably at 20°C to 100°C.

20 Alternative supports for the present invention are non-porous polystyrenes for example divinylbenzene crosslinked polystyrene.

The molar ratio of metallocene complex to ionic activator employed in the method of the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:5000 to 10:1 and most preferred from 1:10 to 10:1.

25 Preferred supported metallocene catalyst systems for use in the process of the present invention include those described in the aforementioned WO 98/27119 and WO 02/06357 as well as those described in our copending applications referenced as BP Cases 9857, 9858 and 9873.

30 Suitable gas phase processes of the present invention include the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and α -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art. Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 and EP 699213 the latter being a

particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the polymerisation of ethylene or the copolymerisation of ethylene and α -olefins having from 3 to 10 carbon atoms.

The present invention will now be further illustrated with reference to the following examples:

Example 1

Catalyst preparation

10 Abbreviations

TEA	triethylaluminium
TiBA	triisobutylaluminium
Ionic Activator A	$[N(H)Me(C_{18-22}H_{37-45})_2][B(C_6F_5)_3(C_6H_4OH)]$
Complex A	$(C_5Me_4SiMe_2N^tBu)Ti(\eta^4-1,3-pentadiene)$

15 Example 1

To a toluene solution of Ionic Activator A (1.2448g, 90.6 μ mol) was added hexane (0.5108g) then TEA in toluene (0.0709g, 155 μ mol). The mixture was left to stand for 30 minutes and was added dropwise to TEA treated silica (3.0238g, 1.4mmolAl/gSiO₂), to which hexane (0.4012g) had been previously added. The silica was agitated during addition and agitation was continued until no lumps were visible. The impregnated silica was allowed to stand at ambient for 1 hour. To a heptane solution of Complex A, (0.4708g 91.8 μ mol) was added hexane (0.3982g). The solution containing Complex A was added dropwise to the Ionic Activator A impregnated silica. The silica was agitated during addition and agitation was continued until no lumps were

25 visible. The impregnated silica was allowed to stand for 1 hour during which time the silica became green. To the silica was added hexane (15ml) and the slurry was agitated to ensure thorough mixing and left to stand at ambient for 30 minutes. Silica was collected by filtration and washed with 2 x 15ml of hexane. Residual hexane was removed under reduced pressure and pumping was continued for 1 hour after
30 fluidisation ceased. The dry green free flowing powder was transferred to a storage bottle and used without further modification.

Polymerisation data

Run conditions

250g of salt as bed

T = 70°C

5 PC2= 6.5Bars.

C6/C2 (pressure ratio) constant at 6700^{-4}

SiO2/TEA impregnated used as scavenger.

H2 added during the gas phase composition (70 ml).

Polymerisation time = 64 min

- 10 0.1 mmol of TiBAO (1M solution in amixture of hexane and pentane) and 1.101g of the above catalyst were premixed (< 1 hour) in a catalyst injection vessel and introduced into the reactor together. At the end of the polymerisation reaction the polymer was separated from the salt by aqueous extraction and dried overnight in an oven. The catalyst activity was 77 g/ghbar and a slowly deactivating profile was observed with an
- 15 instantaneous activity of 60 g/ghbar after 60 min. of polymerisation.

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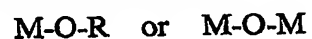
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Claims

1. A gas phase process for the homopolymerisation of ethylene or the copolymerisation of ethylene and α -olefins, said process being carried out in the presence of a metallocene catalyst system comprising (a) a metallocene complex and (b) an ionic activator said process *characterised* in that an organometallic compound of a

5 Group III metal comprising the group



where M is the Group III metal and R is a hydrocarbyl group
is added to the gas phase reactor.

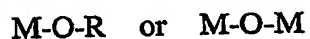
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ABSTRACT
POLYMERISATION PROCESS

A gas phase process for the homopolymerisation of ethylene or the copolymerisation of ethylene and α -olefins carried out in the presence of a metallocene catalyst system comprising (a) a metallocene complex and (b) an ionic activator is characterised in that an organometallic compound of a Group III metal comprising the group



where M is the Group III metal and R is a hydrocarbyl group is added to the gas phase reactor.

Preferred organometallic compounds include aluminoxanes and the process results in improved poison scavenging as well as advantages in activity profiles, catalyst activity and product characteristics.